THE PHOTO-INDUCED REACTION OF BROMINE WITH PHENYLCYCLOPROPANE

by

William Charles Nierman

United States
Naval Postgraduate School

THESIS

The Photo-Induced Reaction
of
Bromine with Phenylcyclopropane

by

William Charles Nierman

June 1969

The Photo-Induced Reaction of Bromine with Phenylcyclopropane

by

William Charles Nierman
Lieutenant (junior grade), United States Navy
B.S., United States Naval Academy, 1968

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the
NAVAL POSTGRADUATE SCHOOL
June 1969

ABSTRACT

Prior studies on the mechanism of the cleavage of cyclopropane and substituted cyclopropane compounds are reviewed and discussed. The rate law for the photolytic reaction of bromine with phenylcyclopropane in concentrations of about 0.02 molar in carbon tetrachloride was determined to be first order in phenylcyclopropane, and half order in bromine and in light intensity. The photoinduced reaction of bromine with a fifteen molar solution of phenylcyclopropane gave 1,1,2,3-tetrabromo-1-phenylpropane as the major product. When this reaction was run using a 1.5 molar solution of bromine and phenylcyclopropane in carbon tetrachloride the product was a mixture of 1,3-dibromo-1-phenylpropane and 1,2-dibromo-1-phenylpropane with the 1,2 isomer predominating. The mechanism of this reaction is discussed.

TABLE OF CONTENTS

ACKNOWLEDGEMENT

The author wishes to express his gratitude to his thesis advisor, Dr. Charles F. Rowell, for his patience and advice and to Mr. Donald W. Moore of the Naval Weapons Testing Center at China Lake for the time and effort spent in running the nuclear magnetic resonance and mass spectra for this study.

I. HISTORY

The study of cyclopropanes is one which has been of interest to organic chemists for a long time. The cyclopropanes occupy the unique position of having reaction characteristics intermediate between the corresponding alkanes and olefins. Since a large amount of strain exists in the small cyclopropane ring it would seem that cyclopropane compounds would be susceptible to all forms of ring opening addition reactions.

Kharasch [1] found that after fifty-two days in the dark at 25° C bromine reacted with cyclopropane only to the extent of 13% and most of the products obtained were substitution products rather than those which would have resulted from a ring opening reaction. Ogg and Priest [2] found that in the presence of light cyclopropane would slowly undergo ring opening with either bromine or iodine to yield the 1,3 addition product exclusively. By raising the temperature to 200° C, substitution products could also be generated in the bromine reaction. Kharasch [1] obtained results with hydrogen bromide which were similar to those obtained with bromine but he noted that oxygen or organic peroxides would catalyze a photochemical chain reaction between bromine and cyclopropane. Chlorine [3, 4] was found to react with cyclopropane to give only addition products without ring opening in both the presence of light and at high temperatures.

This data shows that although the reactions of cyclopropanes are frequently thought to be analogous to the reactions of olefins that this

is clearly not always the case. Under all of the above halogenation conditions ethylene would quickly have reacted to give the addition products almost exclusively.

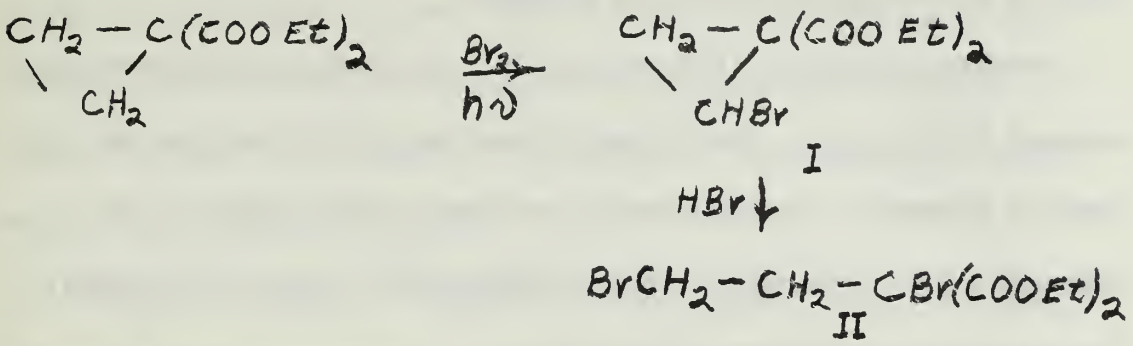
The addition of substituents to a cyclopropane molecule would effect its reactivity in several ways. It would either decrease or increase the electron density in the cyclopropane ring, stabilize the ring by conjugation, or decrease its stability by steric interactions.

Turnbull and Wallis [5] studied the kinetics of the bromination of cyclopropanes which were substituted with carboxyl groups in aqueous acetic acid solutions. A high yield of only the 1, 3 addition products was obtained for these reactions. The mechanism proposed consisted of the formation of an activated complex of unspecified structure (Br_2-cyclopropane) which would collapse to the product.

In his study of alkyl, aryl, and carbonyl substituted cyclopropanes in aqueous systems Kohler [6] found that Markownikoff's rule was followed for the addition reactions with hydrogen bromide and hydrogen chloride. The reactions involve the formation of a carbonium ion transition state and are analogous to the addition reactions with the corresponding olefinic compounds.

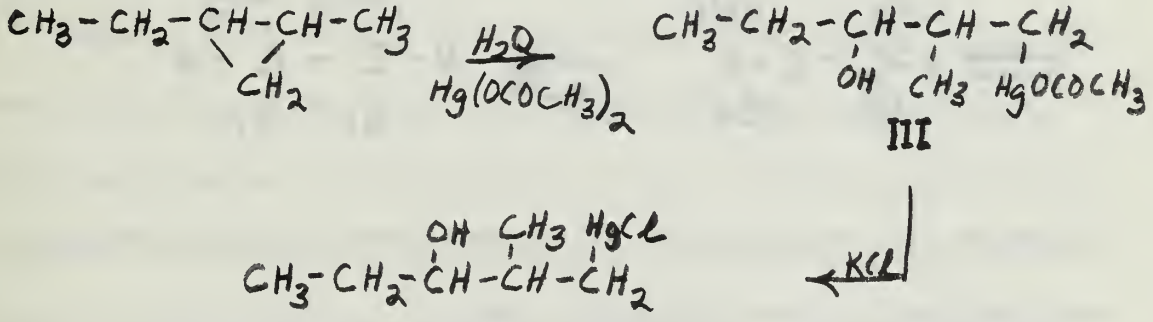
A photochemical study of the bromination of cyclopropane esters [7] was conducted using a high intensity quartz mercury lamp as the light source. The major product in all cases was the 1, 3 addition product but the mechanism involved the addition of hydrogen bromide to

the product of a light induced substitution reaction. This mechanism was verified by the isolation of compound



(I) from the reaction mixture. Treatment of (I) with hydrogen bromide led to essentially complete conversion of (I) to compound (II).

Levina [8] also obtained 1, 3 addition products exclusively in his studies on the ring opening reactions of alkyl cyclopropanes using aqueous mercuric

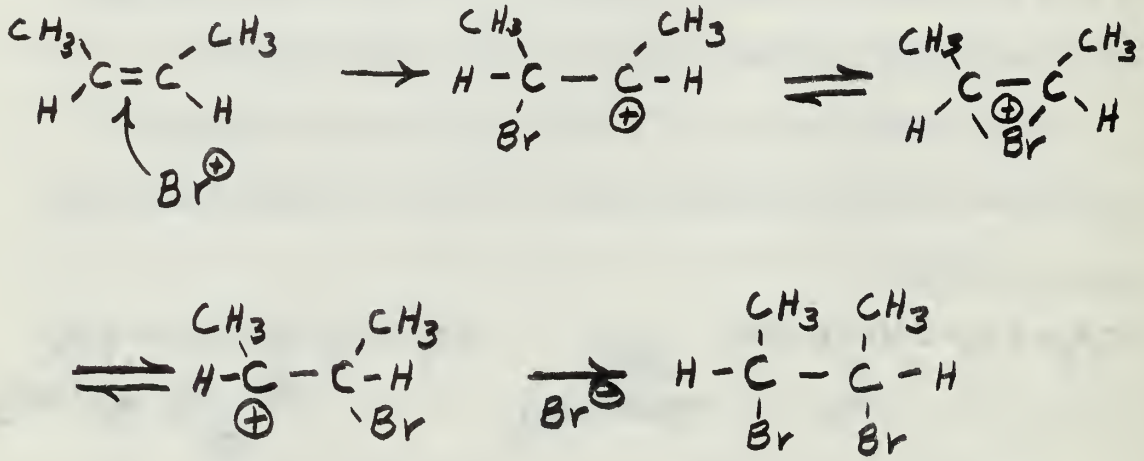


acetate. In this reaction the cyclopropane gave the 1, 3 product (III) which was treated with potassium chloride to give (IV). The rate of the reaction was found to be accelerated by the presence of a greater number of alkyl substituents.

In the polar solvents the effect of alkyl substituents on the reactivity of the cyclopropane ring was comparable to the effect the same substituent would exert on the related olefin. Ingold [9] found that on replacing the four hydrogens of ethylene with methyl groups he

could accelerate the rate of bromine addition in methylene chloride by a factor of fourteen. The rates had intermediate values when only one, two and three methyl groups were present.

Roberts and Kimball [10] first put forth a explanation which would account for this data. They proposed that the rate determining step for bromine addition to a double bond is an electrophilic attack by the bromonium ion on the carbon-carbon double bond. Each of the methyl groups serves to increase the electron



density on the carbon adjacent to the double bond, thereby making it more vulnerable to an electrophilic attack.

In polar solvents it seems that substituted cyclopropanes undergo analogous ring opening reactions, forming carbonium ion transition states. This is supported by the facts that hydrogen bromide adds to the cyclopropane ring according to Markownikoff's rule, the substituents which increase the electron density in the ring also increase the rate of reaction, and all of these ring opening reactions in polar solvents lead exclusively to 1, 3 addition products.

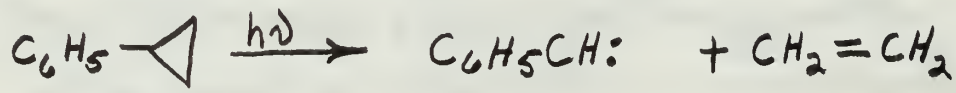
In nonpolar solvents the behavior of cyclopropanes is not as clearly understood. It must be remembered that nonpolar solvents such as carbon tetrachloride do not stabilize the formation of ions so that, in general, reactions which proceed by carbonium ion or carbanion mechanisms will most likely not take place or will proceed at a much reduced rate in these solvents.

Kuivila [11] studied the free radical bromination reaction of some substituted cyclopropanes. He used n-bromosuccinimide to brominate 1-phenyl-2-ethylcyclopropane and 1-phenyl-2-isopropylcyclopropane in carbon tetrachloride but was unsuccessful in generating a reaction until some benzoyl peroxide was present to initiate the reaction. He isolated only the 1, 3 addition product for these reactions.

Hammond and Todd [12] found that several cyclopropane compounds withdrawing substituents were quite unreactive to free radical attacks. Cyclopropylcyanide, methylcyclopropyl ketone, and phenylcyclopropane were inert in attempts at radical propagated polymerization reactions reactions using a variety of free radical initiators. In two of the three compounds studied above, the cyclopropane ring had only one substituent and in all three the electron withdrawing substituents served to decrease the electron density on the ring carbons.

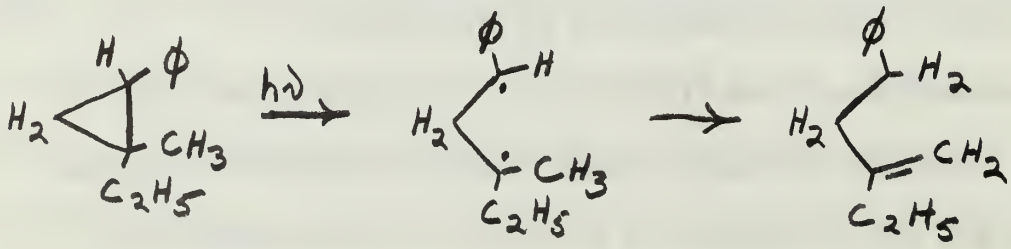
Leermakers and Ross [13] conducted a series of experiments to obtain qualitative information on the stability of phenylcyclopropane to heat and light irradiation. It was found that this compound was thermally stable to temperatures up to 300° C. The major rearrangement

product obtained above this temperature was n-propylbenzene with no detectable formation of polymeric products. Phenylcyclopropane in the gaseous state was decomposed by irradiation with 2573 Å light. This wavelength light was selectively absorbed by the pi electron system of the molecule to give many products and extensive polymerization. It was postulated that the most important primary process was the formation of ethylene and a C_6H_5CH: (methylene). It also noted that there existed a



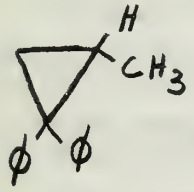
detectable amount of β-methylstyrene in the product mixture.

In a similar study Kristinson and Griffin [14] investigated the photorearrangement of alkyl substituted phenylcyclopropanes in n-hexane and benzene solutions. It was found in all cases that the major reaction was a 1,4 hydrogen transfer process with formation of a terminal olefin. The ring cleavage always occurred between the phenyl substituted carbon and the most alkyl substituted carbon. This would allow a radical intermediate to assume

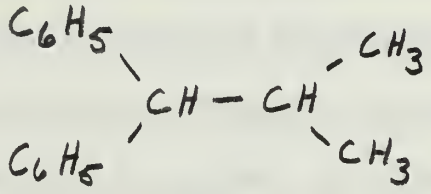


the most stable configuration in both cases.

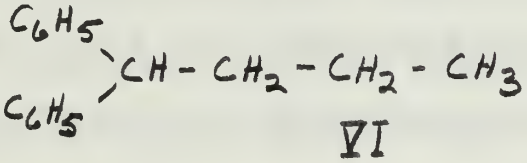
Walborsky [15, 16] studied the cleavage of cyclopropane rings by solutions of sodium in liquid ammonia. It was observed that a cyclopropane ring would be opened quantitatively by solutions of less than 1% metallic sodium dissolved in liquid ammonia if the cyclopropane ring was substituted with a phenyl, carbonyl, carbethoxy or some other group capable of accepting electrons. He found that 1-methyl-2, 2-diphenylcyclopropane would be reduced by sodium in liquid ammonia to 1,1-diphenyl-2-methylpropane (V) and 1,1-diphenylbutane (VI).



$$\xrightarrow{Na/NH_3}$$

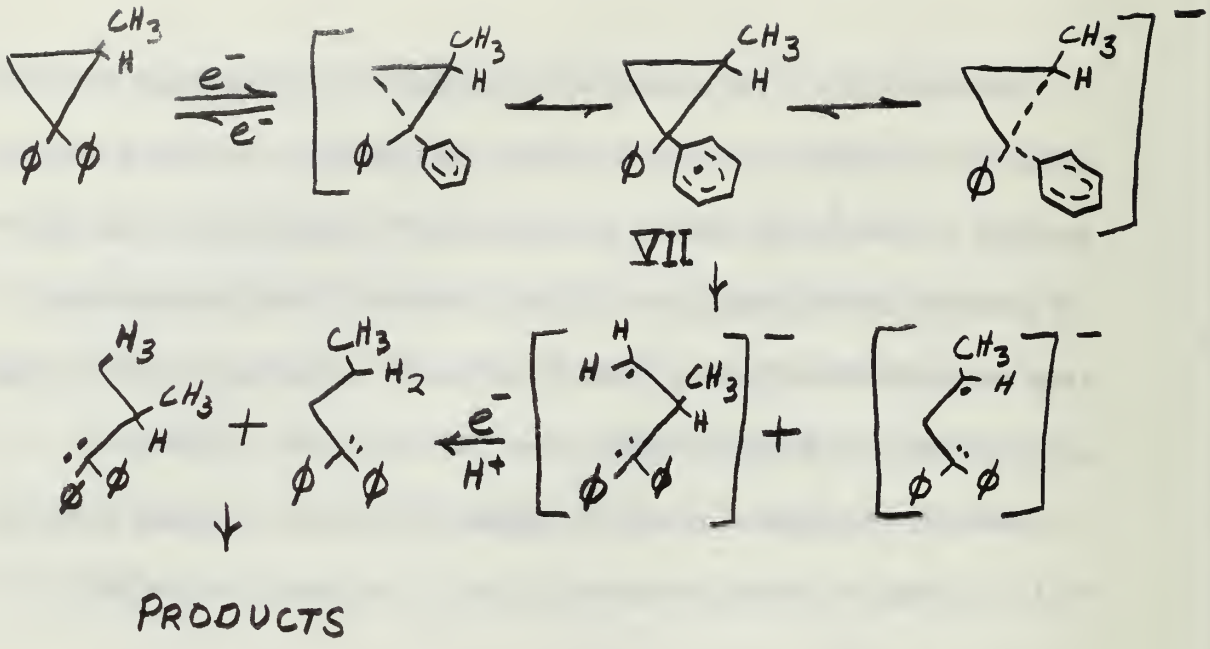


V



VI

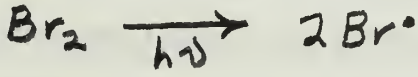
The ratios of (V) and (VI) remained fairly constant over a wide concentration range of sodium which suggests that these compounds resulted from a common intermediate. Consideration of this data led to the proposal of a mechanism initially involving the acceptance of an electron from the sodium by one of the phenyl rings. This mechanism is supported by the fact that at least one

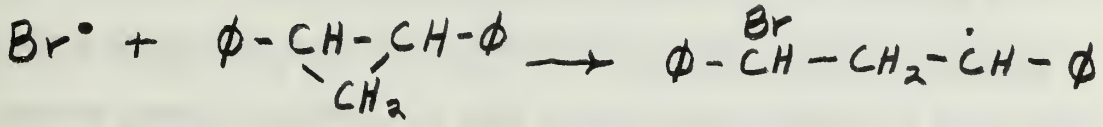


group capable of accepting electrons must be substituted on the cyclopropane before the ring opening reaction will take place under these conditions. The role of the phenyl group in this case is to accept the initial electron from the sodium in liquid ammonia to form the short-lived anion radical species (VII). It is also supported by the fact that carbanion (VIII) was trapped by alkylation with benzyl chloride.

In his studies of the photolytic bromination reaction of 1,2-diarylcyclopropanes Hoffman [17] found that the reaction between bromine and these compounds proceeds smoothly in carbon tetrachloride when exposed to low intensity light with wavelengths between 320 and 450 nm. One mole of bromine is consumed per mole of cyclopropane and the major product of the reaction is 1,3-dibromo-1,3-diarylpropane. These 1,2-diarylcyclopropanes failed to react with bromine in carbon tetrachloride in total darkness indicating that the light-induced ring opening

reaction is a free radical reaction. The rate law for this photo-bromination was determined and the initial steps of the postulated mechanism were the photo-induced formation of atomic bromine followed by the attack of one of these radicals on the cyclopropane ring.





Hoffman used various para-substituted 1,2-diarylcyclopropanes in his rate studies and compared the rates of these relative to those for 1,2-diphenylcyclopropane. The reaction rates were plotted against the Hammett sigma values for the para substituents and in this way a ρ of -0.49 was obtained for this reaction system. The negative ρ indicates that the reaction is accelerated by increased electron density at the reaction site. Therefore, the atomic bromine must be attracted to centers of higher electron density.

Levina [18] conducted a similar study of the bromination of 1,2-diphenylcyclopropane. He used a concentrated solution of bromine and of the hydrocarbon (5 molar) in chloroform to carry out his bromination. Below -7° C most of the hydrocarbon was recovered unchanged and above this temperature it was converted to 1,3-dibromo-1,3-diphenylpropane in two and one-half hours. Levina attempted to brominate 1,2-diphenyl-cyclopropane using n-bromosuccinimide. He placed 0.025 moles of n-bromosuccinimide in 25 ml of dry carbon tetrachloride with 0.15 g of

benzoyl peroxide. The reaction mixture was kept under ultraviolet irradiation for six hours and 96% of the hydrocarbon was recovered unchanged.

It can be concluded from these experimental results that 1,2-diarylcyclopropanes easily undergo free radical ring opening addition reactions but are not vulnerable to electrophilic bromination reactions in nonpolar solvents. This is supported by the ease with which Hoffman opened his 1,2-diarylcyclopropanes with photolytically formed bromine atoms and the fact that no detectable reaction took place under these conditions in the dark. Levina was apparently unaware of the photochemical nature of the reaction of bromine with 1,2-diphenylcyclopropane. His reaction below -7° C was probably conducted in a dark Dewar flask and above this temperature in a lighted laboratory. If this is the case his results are in agreement with Hoffman's. Since n-bromosuccinimide provides only a very small concentration of bromine radicals, the ring opening reaction probably had very little opportunity to proceed to any extent. This indicates that a substantial radical concentration is necessary for the reaction to take place.

Levina [18] also studied the bromination reaction of phenylcyclopropane. He attempted a free radical bromination of phenylcyclopropane with n-bromosuccinimide under conditions identical with those for the same reaction with 1,2-diphenylcyclopropane. As in the previous case he recovered 88% of the unreacted hydrocarbon after six hours of irradiation. It was found that when bromine and phenylcyclopropane

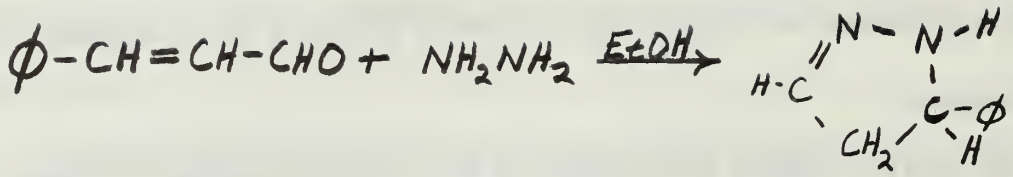
are in a chloroform solution in about five molar concentration that a 75% yield 1-bromo-4-cyclopropylbenzene is formed with essentially no ring opening.

Abbott [19] studied the kinetics of the photobromination of phenylcyclopropane in carbon tetrachloride. He showed that, like 1,2-diarylcyclopropanes, phenylcyclopropane does not react with bromine to a detectable extent in low concentration carbon tetrachloride solutions in the absence of light.

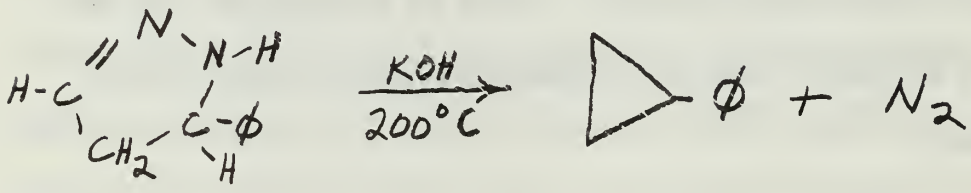
The photobromination of phenylcyclopropane required more study before the reaction could be satisfactorily characterized and a successful discussion made on the difference between the 1,2-diphenyl- and monophenyl- cyclopropane systems. It was for this purpose that this study of the photolytic reaction of phenylcyclopropane with bromine was initiated.

A. SYNTHESIS OF PHENYLCYCLOPROPANE

Of the several methods available [17] for the synthesis of substituted cyclopropanes, the base catalyzed pyrolysis of 5-phenyl-2-pyrazoline was found a satisfactory method for the preparation of the phenylcyclopropane used in this study. The 2-pyrazolines are prepared by the addition of a α,β-unsaturated aldehyde or ketone to a solution of hydrazine in ethanol. To prepare 5-phenyl-2-pyrazoline cinnamaldehyde is added to an alcoholic solution of hydrazine which is kept at 60°C for several hours.



Pyrazolines are unstable in air and it is necessary to store them under a nitrogen atmosphere after they are once synthesized to prevent their oxidation. The pyrazoline can be pyrolyzed in the presence of a small amount of base at a temperature of 200°C to give the corresponding cyclopropane. In this manner 5-phenyl-2-pyrazoline can be used to prepare phenylcyclopropane.



II. EXPERIMENTAL DETAIL

A. PREPARATION OF PHENYLCYCLOPROPANE

The method of Beech [20] for the preparation of phenylcyclopropane was found to be an adequate source for this material. This method utilizes the base pyrolysis of 5-phenyl-2-pyrazoline to yield phenylcyclopropane with some β-methyl styrene as a by-product. The pyrazoline intermediate is unstable in air and was kept under a nitrogen atmosphere. The styrene impurity was removed by polymerization using benzoyl peroxide as an initiator.

1. Preparation of 5-phenyl-2-pyrazoline

Into a three neck 500 ml round bottom flask was placed a mixture of 100 ml of 95% hydrazine and 200 ml of ethanol. This flask was fitted with a reflux condenser and a nitrogen inlet which would maintain a nitrogen atmosphere and stir the solution simultaneously. A separatory funnel was used to add 105.6 g (0.80 moles) of a freshly distilled cinnamaldehyde over the period of an hour while the temperature of the reaction mixture was maintained at 60°C by means of an oil bath. This temperature was maintained for an additional hour and the ethanol was distilled under reduced pressure. The residue was dissolved in 100 ml of ether and washed with 100 ml of water. The ether was dried with anhydrous sodium sulfate and removed by distillation. The residue was placed in a refrigerator under a nitrogen atmosphere for sixteen hours.

The material had solidified in the refrigerator. It was allowed to melt by standing at room temperature for two hours. An oil bath and vacuum system were used to conduct a vacuum distillation of this material. This procedure gave 68.2 g of light yellow crude 5-phenyl-2-pyrazoline over a temperature range of 120-140 C at about 9 mm Hg pressure. The pyrazoline was redistilled under the same conditions. The product, this time a colorless oil, was collected in the temperature range 138-140° C (9 mm Hg). In this manner 60.1 g (51% yield) of the pyrazoline was obtained. $n_D^{26} = 1.5751$; IR peaks C=N stretch 1510 cm^{-1}, C=C aromatic stretch 1610 cm^{-1}, H-H stretch 3300 cm^{-1}.

2. Pyrolysis of 5-phenyl-2-pyrazoline

All of the 5-phenyl-2-pyrazoline collected above was placed in a 100 ml round bottom flask. Three crushed sodium hydroxide pellets were added and the flask was placed in an oil bath and fitted with a condenser. The pyrazoline was then pyrolyzed for 1.5 hours at 200°C. Vacuum distillation of the resultant mixture yielded 19.8 g of a colorless liquid which was obtained over a temperature range of 52-75°C while the pressure varied from 3.0 to 4.3 mm of Hg.

A gas chromatogram of this material was run on an Aerograph Hy-Fi carbowax 20M on 30/60 chromsorb T. The gas flow rates were: air, 400 ml/min, nitrogen, 26 ml/min, and hydrogen, 26 ml/min. The column temperature was 190°C and the injector 250°C. There were two peaks, one at a retention time of 14.5 minutes (β -methyl styrene)

and the other at 23.2 minutes (phenylcyclopropane). The areas under the peaks indicated that about 95% of the product was phenylcyclopropane.

Five grams of benzoyl peroxide was added to the liquid and it was left overnight in an oven at 80°C. Vacuum distillation the next day yielded 15.5 g of material (55.0-41.5/8-2.7 mm Hg). The residue was a viscous brown liquid. Another gas chromatogram indicated that the quantity of impurity had been greatly diminished. Benzoyl peroxide (2.3 g) was added to this distillate and it was again left overnight in an oven at 80°C. Vacuum distillation this time gave only 12.9 g of phenylcyclopropane collected between 54-57°C (6-7 mm Hg). A gas chromatogram this time showed only the phenylcyclopropane peak. This was an overall yield of 13.7% based on the amount of cinnamaldehyde used. $n_D^{23} = 1.5331$; IR peaks C-H stretching, cyclopropane 3000 cm^{-1}; NMR peaks (in ppm) a complex multiplet centered at 0.70, a quintet centered at 1.81, and a sextet centered at 7.00; relative areas 4:1:5.

Element Analysis

	C %	H %
Calculated	91.50	8.50
Found	91.37	8.45

B. THE PHOTOLYSIS REACTION OF BROMINE WITH PHENYLCYCLOPROPANE

The visible and ultraviolet spectra of bromine and phenylcyclopropane were taken in carbon tetrachloride solutions. The phenylcyclopropane was found to absorb strongly in the range of 210 nm to 300 nm. It did not absorb significantly above 300 nm. Bromine absorbed strongly in the range 350 to 550 nm.

Ten grams of phenylcyclopropane was added to 30 ml of carbon tetrachloride in a 125 ml pyrex erlenmeyer flask. Bromine was added with an eyedropper until the color of the bromine would remain for more than a few seconds. The flask was located about two feet from a 500 watt tungsten light source. In the initial few minutes of the reaction a great deal of heat was evolved. Hydrogen bromide (a chocking white gas which turned moist litmus red) was produced through the entire course of the reaction. It was necessary to continue adding small amounts of bromine to maintain the bromine color and hydrogen bromide evolution over the four day period required for the reaction to go to completion. The reaction which had initially proceeded rapidly took a very long time to reach completion.

After the four days of irradiation a thin layer chromatogram was taken using a 1/2 mm plate and 80% benzene, 20% heptane as the solvent. Development of the plate with aqueous formaldehyde solution and concentrated sulfuric acid showed the presence of only one aromatic component.

The carbon tetrachloride was distilled off at reduced pressure. The residue was dissolved in 25 ml of ether and washed with an aqueous solution of sodium thiosulfate. The ether was removed on a hot plate and 36.4 g of a red liquid remained. After remaining in the refrigerator for a day the red liquid became a yellow solid. A small amount of this material was dissolved in carbon tetrachloride and a gas chromatogram was run using an Aerograph Hy-Fi model 600C with a column of 5% carbowax 20M on 30/60 chromsorb T at a column temperature of 200°C and an injector temperature of 250°C. This gas chromatogram showed two peaks with the ratio of the areas about nine to one.

An alumina chromatographic column was used to separate the components of the product. A buret was filled half full on 30-60° pteroleum ether and a small plug of cotton was pushed to the bottom with a long piece of glass tubing. About an inch of clean sand was placed on top of the plug and 35 g of aluminium oxide (active neutral, activityI) was poured on top of this. Another inch of sand completed the preparation of the column.

Into a 50 ml erlenmeyer flask was placed 1.5 g of the product and 10 ml of a 50% solution of ether-petroleum ether was added. The resulting solution was placed on the column and samples were taken at 25 ml increments. With 50% ether-petroleum ether as the elutant, a significant amount of white crystals were obtained with 50 ml of this solvent. A small amount of a yellow oil was also eluted from the column after 75 more ml of 100% methanol was used as the elutant.

The remainder of the material was dissolved in 25 ml of ether and was placed on the column. A large quantity of white crystals was obtained after 50 ml of elution with 50% ether-petroleum ether. There were apparently two more components on the column distinguishable by color. The elutant was changed to 100% methanol and both bands moved down the column at the same rate. These components were collected separately and stored in the methanol solutions in a refrigerator. The white crystalline solid was recrystallized twice from hot petroleum ether but a yellow tinge remained in the material. This was removed by recrystallization from 35 ml of hot methanol to yield 4.8 g of a pure white crystalline compound. M. P. 78.5°C.

The mass and nuclear magnetic resonance spectra of the white solid compound isolated from the photogromination reaction was taken. The mass spectrum showed a parent peak at 436 mass units suggesting a molecular formula of $C_9H_8Br_4$. The NMR showed the presence of five aromatic protons and three others. There were three doublets of doublets centered at 3.7, 4.5, and 4.8 ppm and two complex aromatic multiplets at 7.1 and 7.6 ppm. The area ratios for these absorbances were respectively 1:1:1:3:2.

An attempt was made to remove the methanol from the second fraction from the column by means of a rotary evaporator. This was discontinued as the compound became darker when it was necessary to heat the solution with hot water. The infrared spectrum of the second and third components from the column showed them to be the

same compound or compounds. To the methanol solution was added 25 ml of ether and the solution was extracted several times with water. The ether was dried with anhydrous sodium sulfate and removed from the product by means of a rotary evaporator. Only a very small amount of a yellow oil was obtained (0.092 g). The infrared spectrum of this material showed a strong carbonyl band at 1750 cm^{-1}.

To 0.172 g of magnesium, which had been heated in an oven at 100°C for several days, was added 0.767 g of the previously identified tetrabromoproduct. This mixture was placed in a dry 50 ml round bottom flask that was fitted with a reflux condenser and 15 ml of freshly opened anhydrous ether was added. A few of the magnesium turnings were crushed with a dry stirring rod. The solution immediately became cloudy and evolved heat. The heat generated supported reflux for thirty minutes. The reaction was refluxed on an oil bath for an additional sixty minutes and the solution in the flask was decanted away from the excess magnesium into a 125 ml erlenmeyer flask. The magnesium was washed with ether, dried and weighed (0.104 g remained). Ten ml of methanol was added to the ether solution causing a highly exothermic formation of a cloudy precipitate. To this was added twenty ml of water. Two drops of phenolphthalein was added but the solution did not turn pink. Five drops of 0.1 M potassium chromate was added and the mixture was titrated with 0.2 M silver nitrate. The solution remained yellow until 26.75 ml of the silver

nitrate was added. Calculations from this titration assuming a molecular formula of $C_9H_8Br_4$ indicated that three bromine atoms per propane molecule were removed by the magnesium.

The ether layer which remained after the silver nitrate titration was removed with an eyedropper and dried with anhydrous sodium sulfate. The ether was removed on a rotary evaporator leaving a yellow solid material. The nuclear magnetic resonance spectrum of this material showed strong absorbance at 7.0 ppm indicating the possible presence of a terphenyl. An infrared spectrum also showed a strong band at 1590 cm^{-1}, a possible ethylenic or C=C aromatic stretching frequency.

C. THE PHOTOLYSIS REACTION AT LOWER CONCENTRATIONS

Into a 500 ml pyrex erlenmeyer flask was placed 1.784 g of phenylcyclopropane (0.150 mole) and 100 ml of carbon tetrachloride. To the resulting solution was added 175.7 ml of 0.085 molar bromine solution in carbon tetrachloride (0.0150 mole). A magnetic stirrer was used as the flask was radiated with a 60 watt microscope illuminator using a collimating lens. The reaction required about sixty hours to go to completion as indicated by repeated constant absorbance of the solution on a Beckman DU Spectrophotometer at 410 nm.

The carbon tetrachloride was removed by distillation at reduced pressure leaving 4.62 g of a dark colored liquid. A gas chromatogram was run using the Aerograph Hy-Fi with the previously described 5%

carbowax 20M column and the same gas flow rates with a column temperature of 100°C and an injector temperature 50° higher. There were two product peaks at retention times of 11 and 12 minutes. The material was found to evolve a choking white gas (hydrogen bromide) upon standing. An infrared spectrum showed peaks at 690 and 750 em^{-1} indicating the presence of only monosubstituted aromatic products.

Into a 25 ml erlenmeyer flask was placed 1.433 g of the product material and to this was added 10 ml of ether. Five ml of freshly distilled pyridine was added to this solution and it was left overnight. A viscous water soluble brown mass was produced in the bottom of the flask. The pyridine was removed from the ether by washing eight times with water. The ether was dried with sodium sulfate and removed on a rotary evaporator. A gas chromatogram and infrared spectrum indicated that the recovered material was not significantly changed by this process.

A chromatographic column was prepared using petroleum ether and 35 g of aluminum oxide. Onto this column was directly placed 0.903 g of the liquid product and the column was eluted with 50% petroleum ether-ether. A significant quantity of a light yellow liquid was eluted after 30 ml of solvent was used. The solvent was removed from this material and the elutant was changed to 50% methanol-ether. After 30 ml of this solvent a minute amount of a viscous dark colored oil was obtained.

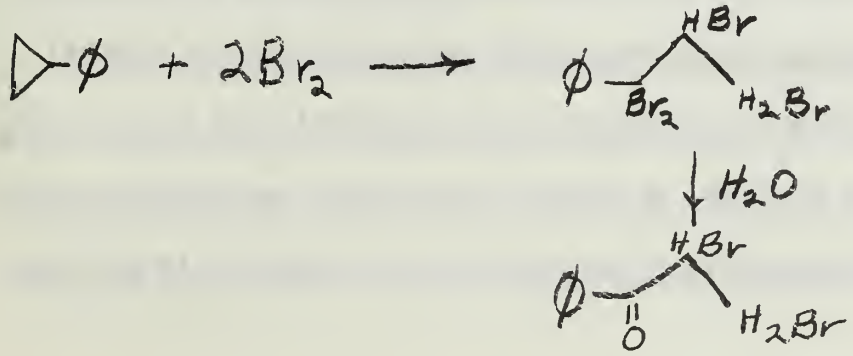
A nuclear magnetic resonance spectrum of the light yellow oil was taken. The spectrum contained several weak lines in the region of 0.9 ppm (§). There were strong doublets centered at 1.6 and 1.9 ppm. The peaks at 1.9 were very strong. Complex multiplets were observed to be centered at 2.5, 3.4, 4.5, 5.1, and 7.4 ppm.

D. THE KINETICS OF THE PHOTOGROMINATION REACTION

All of the kinetics measurements were taken on a Beckman DB Spectrophotometer using bromine absorption wavelengths of 470 nm (ϵ =128.10), 410 nm (ϵ =190.05), 500 nm (ϵ =91.02), 536 nm (ϵ =55.4), and 560 nm (ϵ =20.14). The reaction solutions were carefully measured into standard one cm pyrex cells and the cells were placed on the circumference of a circle of radius 12 or 24 inches from a Hanovia number 7654-1, 250 watt mercury lamp behind a Corning filter (#5113) which transmitted light in the range 370 to 450 nm. This filter and the pyrex cells assured that only the bromine was activated by the mercury lamp. The concentration for both bromine and phenylcyclopropane ranged from 0.0013 molar to 0.08 molar. All runs contained either an equal concentration of both bromine and phenylcyclopropane or a ten fold excess of one or the other (cf. Appendix). Carbon tetrachloride was used as the solvent in all cases and the reactions were run at room temperature (about 24°C). At timed intervals the light source was covered and the absorbance of the solutions was measured. This data was plotted using the integrated forms of various rate laws to establish the rate law for this reaction.

III. DISCUSSION

Before beginning this discussion it is necessary to state some of the experimental results in detail. In the first reaction studied elemental bromine was added to a fifteen molar solution of phenylcyclopropane in carbon tetrachloride. The solution was in a pyrex erlenmeyer flask two or three feet from a 500 watt tungsten light source. The pyrex served to a certain extent to filter out ultraviolet radiation which would have caused rearrangement of the phenylcyclopropane to an olefin and the carbon tetrachloride provided a medium for the reaction which would minimize any ionic processes which would compete with the expected free radical reaction. The reaction was extremely slow. Four days were required for the reaction to go to completion under the intense visible radiation provided by the tungsten lamp. The major product (90%) determined from nuclear magnetic resonance and mass spectra was 1,1,2,3-tetrabromo-1-phenylpropane ($C_6H_5CBr_2CHBrCH_2Br$). The minor product was assumed to be 2,3-dibromo-1-phenylpropane-1-one which was formed from the major product in the work up of this material. This assumption was made on the basis of a strong carbonyl absorption band in the infrared spectrum of this material.

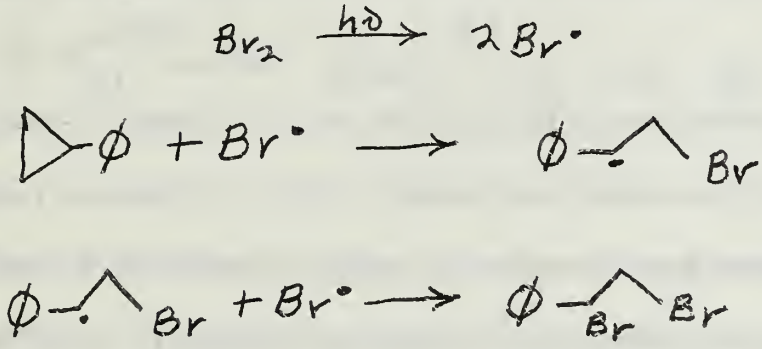


This data indicates that in addition to undergoing a ring opening reaction with bromine in carbon tetrachloride, phenylcyclopropane also experiences a large amount of substitution. One or both of these processes taking place is very slow as the reaction required such a large amount of time to go to completion. Since the reaction used carbon tetrachloride as the solvent, all of the major processes taking place between phenylcyclopropane and bromine were likely radical in nature. A visible light source was used and the reaction vessel was pyrex, making it therefore possible that the product was formed as the result of attacks by photo-induced bromine radicals. However, since pyrex is not a perfect filter between 210 and 300 nm where phenylcyclopropane absorbs and because the time involved is so great this interpretation cannot be assumed.

A similar reaction that was run at lower concentrations of bromine and phenylcyclopropane gave results that were different. A carbon tetrachloride solution of 1.5 molar phenylchclopropane and bromine in a pyrex flask was irradiated using a 60 watt microscope illunimator. The reaction this time required sixty hours to go to completion. The major portion of the product (95.5%) was isolated by column chromatography and a nuclear magnetic resonance spectrum of this material was obtained in order to determine the composition of this material. The spectrum showed peaks which were interpreted to be due to $-CH_2$, CH_2Br-, CH_3-, α -CHBr, β -CHBr, cyclopropyl-, and phenyl protons. The area under the methyl proton peaks was considerably larger than

that under the CH_2Br- peaks. The isolated solution was apparently a mixture of largely 1-phenyl-1,2-dibromopropane and 1-phenyl-1, 3-dibromopropane with the 1,2 isomer predominating. Some phenyl-cyclopropane was apparently also present in the mixture.

Once again it is obvious that more than one process is taking place simultaneously in this reaction. The 1,3-dibromo-1-phenylpropane is undoubtedly the product of the homolytic opening of the cyclopropane ring by photo-induced bromine free radicals. The following mechanism is suggested as the most probable: Bromine radicals are formed by the irradiation of bromine molecules with visible light followed by an attack on one of the non-benzyl carbons of the cyclopropane ring by a bromine radical to form radical species (I). This radical is then



destroyed by the addition of another bromine radical to form 1,3-dibromo-1-phenylpropane.

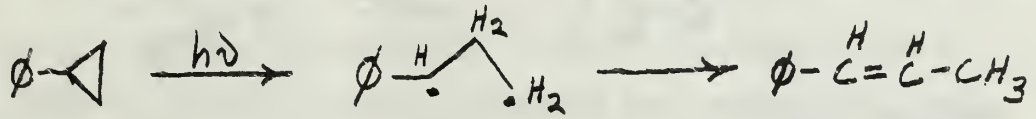
There are several reasons to assume that the bromine radical will not attack the benzyl carbon of the cyclopropane ring. After the attack on a non-benzyl carbon to open the ring, the electron in the radical transition state would find itself on a secondary carbon stabilized by

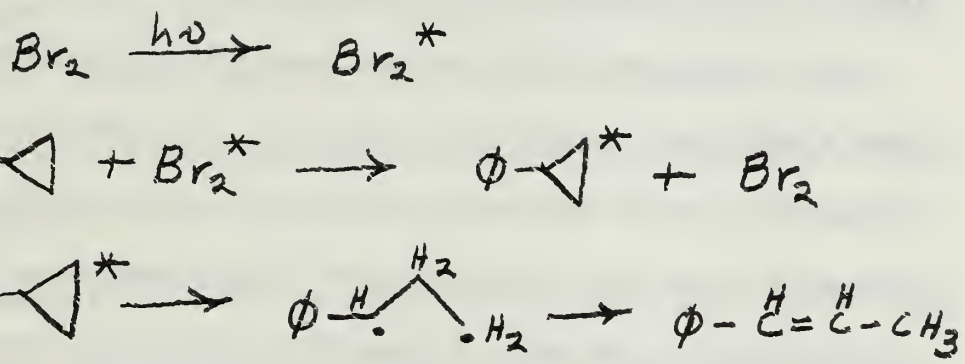
a phenyl group and a methylene group. This would be the thermodynamically most stable transition state for the free radical ring opening process. Since this path has a lower energy barrier to the reaction, it will proceed to a greater extent by this mechanism.

The benzyl carbon is also the most sterically hindered site for bromine attack in addition to providing the most stable site for the unpaired electron in the radical transition state. This benzyl carbon is bonded to a phenyl group, two other carbons and a hydrogen which could provide hindrance to the approach of a large bromine atom. Therefore, it would react at the other sites in the absence of any other considerations. In light of these considerations for the radical ring opening reaction of phenylcyclopropane this reaction pathway seems favored.

Under the conditions of the reaction the 1,3-dibromo-1-phenylpropane was not the predominant product. The 1,2-dibromo- isomer was present in the product mixture in greater quantity and a small amount of unreacted phenylcyclopropane also remained. Since the reaction took sixty hours for completion and some of the phenylcyclopropane remained unchanged, it can be said that phenylcyclopropane is relatively inert to attack by bromine radicals when compared to the reactivity of 1,2-diarylcyclopropanes [17] under similar conditions. In light of the discussion of the reaction pathway to the formation of the 1,3-diabromo- isomer, the 1,2-dibromo- product can only be explained as the result of either photolytically induced rearrangement

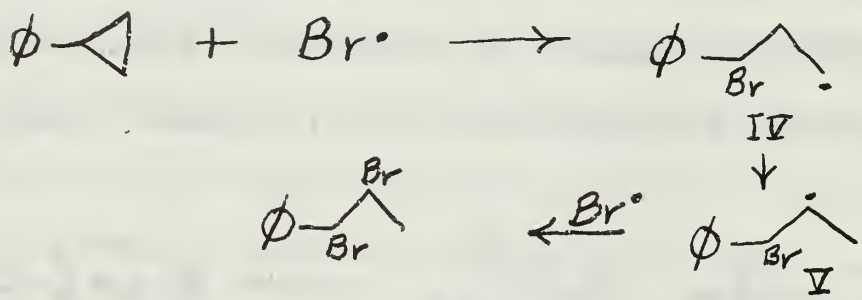
of phenylcyclopropane to β-methylstyrene (II) or a photosensitized rearrangement (III) where bromine in an excited state would transfer its energy to a phenylcyclopropane molecule which would then rearrange with hydrogen transfer to β-methylstyrene. Bromine would quickly add to the β-methylstyrene to give 1,2-dibromo-1-phenylpropane.

II 

III 

The rearrangement of phenylcyclopropane to β-methylstyrene is supported by the fact that Leermakers and Ross [13] obtained a detectable quantity of β-methylstyrene among the products of the gas phase photo-decomposition of phenylcyclopropane. This rearrangement is also the lowest energy route to the formation of the 1,2-dibromo-isomer. In almost all cases the radical ring opening reactions of the cyclopropanes the 1,3 addition compound is obtained as the major product [17, 11, 18]. In order to obtain 1,2-dibromo-1-phenylpropane from a bromine radical ring opening reaction, energetically unfavorable

steps would have to take place. The bromine radical would have to attack the benzyl carbon forming the energetically unfavorable radical (IV). This radical would have to undergo a hydrogen transfer to (V)



which would result in the formation of the 1,2-dibromo- product. Neither of the processes would be energetically favored.

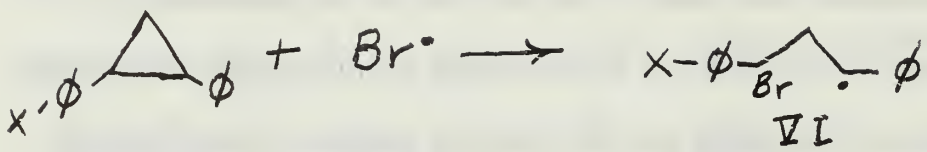
This reaction was conducted in a pyrex erlenmeyer flask using about a sixty watt tungsten light source. These conditions and the fact that the reaction took such a long time to reach completion suggests that the rearrangement of phenylcyclopropane was caused by ultraviolet light generated to a moderate extent by the tungsten lamp and leaked at a very slow rate through the pyrex reaction vessel to be absorbed by the phenylcyclopropane. If the bromine were acting as the photosensitizer for this rearrangement the reaction would have proceeded at a much faster rate due to the bromine concentration and the intensity of the light in the region of bromine absorbance. Even under the conditions of the reaction the rearrangement was faster than the free radical ring opening process since the 1,2 isomer was present in the product to a greater extent than the 1,3 isomer.

The question still remains as to why 1,2-diarylcyclopropanes smoothly undergo radical ring opening reactions to yield 1,3-addition

products exclusively while under the same conditions phenylcyclopropane is comparatively inert to radical ring opening reactions. In order to answer this question it is necessary to investigate the various possible effects involved in the two reaction systems. Looking first at the steric considerations it is observed that the bromine easily attacks the most sterically hindered site of the most sterically hindered molecule, 1,2-diphenylcyclopropane, while it is extremely slow in opening the least sterically hindered of the two compounds, phenylcyclopropane. Ring opening of 1,2-diphenycyclopropane occurs between the two most substituted carbons so it can be concluded that steric considerations are of no importance in causing the differences in these two systems.

In looking at the inductive effects of the substituents on the cyclopropane ring it must be remembered that although the phenyl group is an electron withdrawing substituent, the electrons of the carbon-carbon bonds of the cyclopropane ring have the ability to conjugate with the pi electron system of the phenyl group. This means that the phenyl group is capable of donation electron density to the cyclopropane ring. Hoffman [17] found that increased electron density on the substituted carbons of the cyclopropane ring causes the rate of the ring cleavage reaction by atomic bromine to increase. The reaction would be increased either by stabilization of the radical transition state (VI) formed immediately after the ring was opened or by increasing the frequency with which a bromine atom attacks and opens

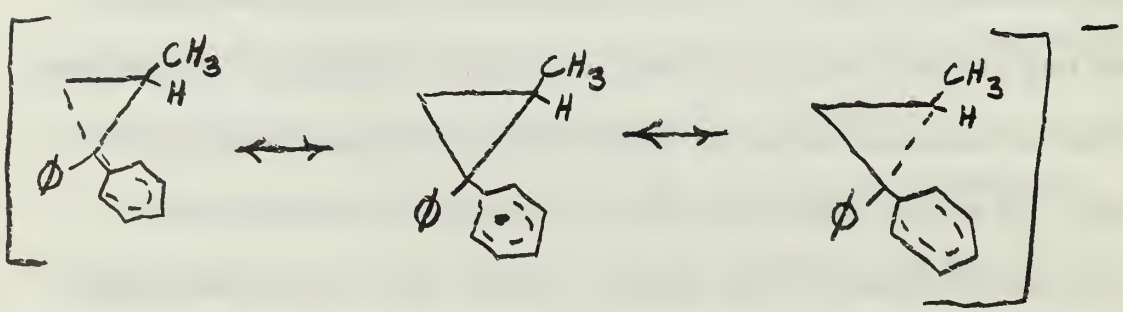
the cyclopropane ring. Since increased electron density at the free



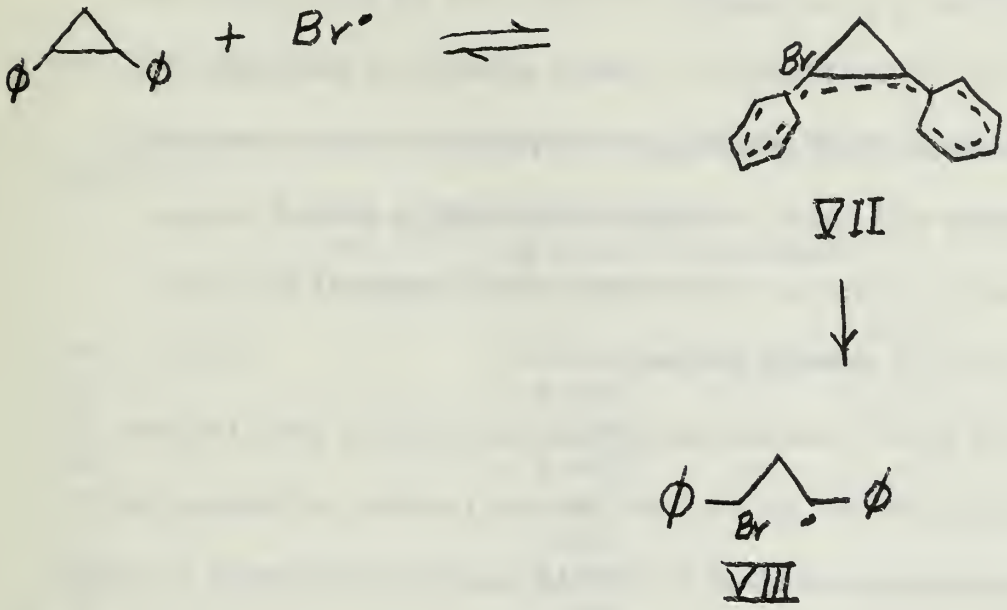
VII

radical site would only serve to make the radical less stable it is likely that the bromine attacks in an electrophilic manner. Increasing the electron density at a substituted carbon would increase the frequency of bromine radical attacks at that site, thereby increasing the rate of the overall reaction. Investigation of this effect offers little understanding as to why phenylcyclopropane is relatively inert to attack by bromine radicals for the cyclopropyl group of phenyl-cyclopropane is conjugated to a phenyl ring and is therefore capable of having its electron density increased by this stustituent.

To gain this understanding, effects which can be designated as general electronic considerations should be investigated. Walborsky [15, 16] observed that a cyclopropane ring would be opened by sodium in liquid ammonia only if it was substituted with a group capable of accepting an initial electron from the sodium to form a transition state as indicated. For the bromination of 1,2-diphenylcyclopropane a



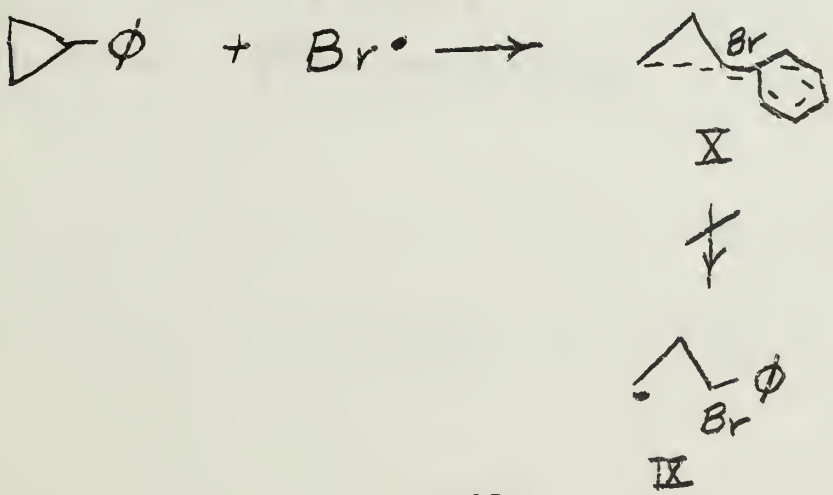
similar transition state (VII) can be proposed which would generate



VII

VIII

the radical transition state (VIII). It must be understood that in effect the bromine radical attacks the benzyl carbon, causing its electron to be placed in the conjugated pi system of the phenyl group and the cyclopropane ring. Phenylcyclopropane could also form a transition state analogous to (VII) but this state would most likely return to its original configuration because radical (IX) would be a much higher energy state than would (VIII) because structure (IX) is a primary free radical not stabilized by any substituents.



X

IX

For the ring opening to take place from transition state (X) it is necessary that a group capable of stabilizing the free radical transition state be substituted on a carbon adjacent to the phenyl substituted carbon. This is perhaps an explanation why 1,2-diphenylcyclopropane will easily undergo ring opening by radical bromine attacks under conditions which phenylcyclopropane is relatively inert to this ring opening process.

For the sake of completeness it is necessary to state that the experimental rate law for the light induced reaction of bromine with phenylcyclopropane in about 0.02 molar carbon tetrachloride solutions was:

$$\text{rate} = k\ (\triangledown)\ (Br_2)^{1/2}\ (I)^{1/2}$$

Since the product analysis showed that more than one process was taking place during the reaction it would not be meaningful to attempt to extract mechanistic information from this rate law since the product data was obtained at a considerably higher concentration where a change in mechanism is very likely.

APPENDIX A

SAMPLE TREATMENT OF KINETIC DATA

To determine the overall rate of the reaction of the solution contained:

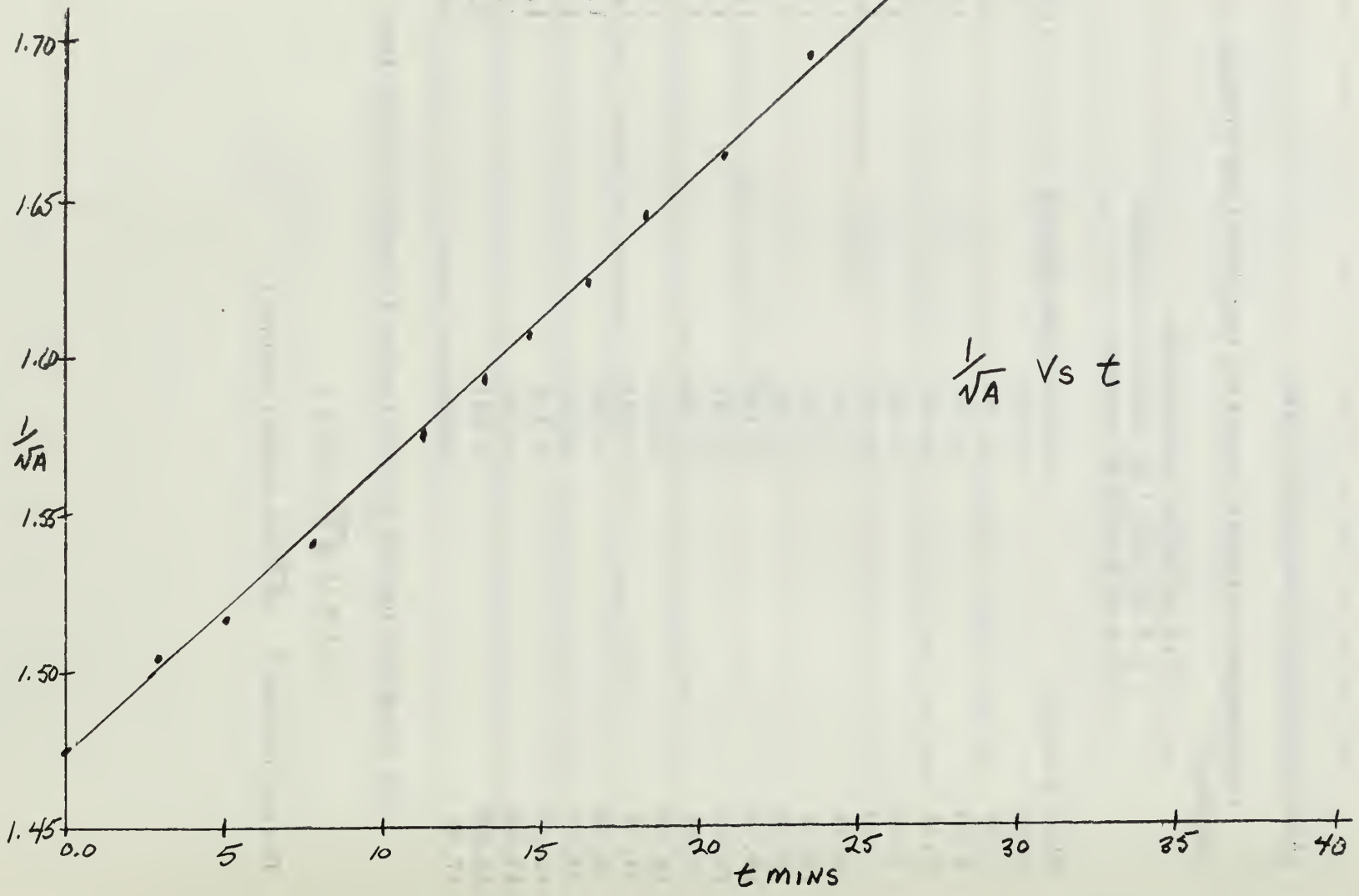
0.2 ml carbon tetrachloride
1.4 ml 0.0211 M phenylcyclopropane
1.4 ml 0.0178 M bromine

Time (minutes)	Absorbance (at 530 nm)	$1/\sqrt{A}$
0.00	0.460	1.475
1.01	0.453	1.484
2.00	0.450	1.490
3.01	0.447	1.495
4.10	0.440	1.506
7.10	0.424	1.536
10.01	0.410	1.562
13.01	0.393	1.597
16.03	0.379	1.626
19.00	0.363	1.661
22.02	0.347	1.698
25.01	0.326	1.751
28.00	0.314	1.786
31.01	0.301	1.821
34.06	0.289	1.862
37.04	0.275	1.908
42.01	0.256	1.976
47.00	0.239	2.049
52.00	0.221	2.128
57.02	0.205	2.208

The integrated form of the rate law for 2/3 order is of the form:

$$1/A = 1/\sqrt{A} + 1/2\ k\ t$$

To test this law $1/\sqrt{A}$ was plotted against t.


1.70
1.65
1.60
1.55
1.50
1.45
1/√A
0.0
5
10
15
20
25
30
35
40
t MINS
1/√A Vs t

BIBLIOGRAPHY

1. Kharasch, M. S., Fineman, M. Z., and Mayo, F. R., J. Am. Chem. Soc., 61, 2139 (1939).

2. Ogg, R., Jr., and Priest, W., J. Am. Chem. Soc., 60, 217 (1938).

3. Roberts, J. D., and Dristine, P. H., J. Am. Chem. Soc., 67, 1281 (1945).

4. Stevens, P. G., J. Am. Chem. Soc., 68, 620 (1946).

5. Turnbull, J. H., and Wallis, E. S., J. Org. Chem., 21, 663 (1956).

6. Kohler, E. P., and Connant, J. B., J. Am Chem. Soc., 39, 1404 (1917).

7. Nicolet, B. H., and Sattler, L. J., J. Am. Chem. Soc., 49, 2066 (1927).

8. Levina, R. Ya., Kostin, V. N., and Tartakowsky, V. A., Zhur. Obschlei Khim., 26, 3339 (1956).

9. Ingold, K. C., and Ingold, E. H., J. Chem. Soc., 1931, 2354.

10. Roberts, I., and Kimball, G. E., J. Am. Chem. Soc., 59, 947 (1937).

11. Kuivila, H. G., Caywood, S. C., Bayce, W. F., and Langevin, F. L., Jr., and Langevin, F. L., Jr., J. Am. Chem. Soc., 77, 5175 (1955).

12. Hammond, G. S., and Todd, R. W., J. Am. Chem. Soc., 78, 4081 (1954).

13. Leermakers, P. A., and Ross, M. E., J. Org. Chem., 31, 301 (1966).

14. Kristinson, H., and Griffin, G. W., Tetrahedron Letters, 28, 3259 (1966).

15. Walborsky, H. M., and Pierce, J. B., J. Org. Chem. 33, 4102 (1968).

16. Walborsky, H. M., Johnson, F. P., and Pierce, J. B., J. Am. Chem. Soc., 90, 5222 (1968).

17. Hoffman, J. M., Ph. D. Thesis, Naval Postgraduate School (1966).

18. Shabarov, Yu. S., Burenko, S. N., and Levina, R. Ya., Zhur. Obschehei Khim., 38, 61 (1968).

19. Abbott, W. A., M. S. Thesis, Naval Postgraduate School (1968).

20. Beech, S. G., Turnbull, J. H., and Wilson, W., J. Chem. Soc., 1952, 4686.

21. McGreer, D. E., J. Org. Chem., 25, 852 (1960).

22. McGreer, D. E., et. al., Can. J. Chem., 43, 1407 (1965).

23. McGreer, D. E., et. al., Can. J. Chem., 43, 1398 (1965).

24. Frost, A. A., and Pearson, R. G., Kinetics and Mechanism, John Wiley and Sons, Inc., 1953.

25. Levina, R. Ya., Shabarov, Yu. S., and Potapov, V. K., Zhur. Obschehei Khim., 29, 3233 (1959).

26. Shabarov, Yu. S., Levina, R. Ya., Potapov, V. K., Osipov, A. M., and Treshchova, E. G., Zhur. Obschehei Khim., 30, 3874 (1960).

27. Bernett, W. A., J. Chem. Ed. 44, 17 (1967).

28. Gordon, A. J., J. Chem. Ed., 44, 461 (1967).

29. Walsh, A. D., Trans. Faraday Soc., 45, 179 (1949).

INITIAL DISTRIBUTION LIST

		No. Copies
1.	Defense Documentation Center Cameron Station Alexandria, Virginia 22314	20
2.	Library Naval Postgraduate School Monterey, California 93940	2
3.	Commander, Naval Ordnance Systems Command Headquarters, Department of Navy Washington, D. C. 20360	2
4.	Professor Charles F. Rowell Department of Material Science and Chemistry Naval Postgraduate School Monterey, California 93940	2
5.	LT(j.g.) William C. Nierman 1605 S. Flower St. Santa Ana, California 92707	2

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Naval Postgraduate School Monterey, California 93940	UNCLASSIFIED
	2b. GROUP

3 REPORT TITLE

The Photo-Induced Reaction of Bromine with Phenylcyclopropane

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Master's Thesis; June 1969

5 AUTHOR(S) *(First name, middle initial, last name)*

William Charles Nierman

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
June 1969	43	29

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Naval Postgraduate School Monterey, California 93940

13. ABSTRACT

Prior studies on the mechanism of the cleavage of cyclopropane and substituted cyclopropane compounds are reviewed and discussed. The rate law for the photolytic reaction of bromine with phenylcyclopropane in concentrations of about 0.02 molar in carbon tetrachloride was determined to be first order in phenylcyclopropane, and half order in bromine and in light intensity. The photo-induced reaction of bromine with a fifteen molar solution of phenylcyclopropane gave 1,1,2,3-tetrabromo-1-phenylpropane as the major product. When this reaction was run using a 1.5 molar solution of bromine and phenylcyclopropane in carbon tetrachloride the product was a mixture of 1,3-dibromo-1-phenylpropane and 1,2-dibromo-1-phenylpropane with the 1,2 isomer predominating. The mechanism of this reaction is discussed.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Phenylcyclopropane						
Bromine						
Cyclopropane						
Photochemicalbromination						
Brominative cleavage						